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Model Filled Polymers III. Rheological Behavior of Polystyrene
Containing Crosslinked Polystyrene Beads

by

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ABSTRACT

The steady shear viscosity and dynamic moduli, at 180 and 200°C, of polystyrene composites, containing crosslinked monodisperse polystyrene beads varying in diameter from 0.2 to 0.8 μm , are independent of bead size and crosslink density, but increase with the volume fraction of beads. Steady shear viscosities exhibit power law regions up to 40% concentration of beads, but no yield stress. Storage and loss moduli are initially linear with frequency, on double logarithmic plots, with limiting slopes of 1.3 and 0.9, respectively. Uncrosslinked beads and beads crosslinked with 0.1% divinylbenzene are destroyed by thermomechanical dispersion in the melt.

Model Filled Polymers

III. Rheological Behavior of Polystyrene Containing Crosslinked Polystyrene Beads

INTRODUCTION

The technological importance of filled polymer systems is well recognized [1-3]. Elastomers, plastics, and composites contain polymeric components which, in the pure state, are often commercially useless. Studies of the viscoelastic properties of filled polymers are of considerable scientific and practical significance [4]. The processing of such materials to form desired structures is essential for commercial application. A basic understanding of the flow behavior, or rheology, of filled polymers will permit control and optimization of processing conditions. Here, viscoelastic studies in the "terminal zone," or melt flow region of the viscoelastic spectrum, elucidate the rheological response.

Recently, we reported on the rheological behavior of model systems for the toner in the electrophotographic process [5-9]. Commercial toners are pigmented particles used to develop a latent image in printing or copying and are often copolymers of styrene and butyl methacrylate containing a carbon black filler. We measured the shear stress as a function of shear rate in steady shear flow on rotating the cone in a cone and plate geometry, with a Weissenberg rheogoniometer, for polymer melts containing carbon blacks with a wide range of surface areas [5-7]. In addition, we studied the dynamic mechanical behavior of these systems in the cone and plate geometry by sinusoidal oscillation of the cone at selected frequencies and a strain amplitude of 5% [8, 9]. Polymers included high and low molecular weight polystyrene and polybutyl methacrylate, as well as random copolymers of styrene and butyl methacrylate. For polymers containing carbon black, both the relative viscosity (compared to the pure polymer) and the dependence of viscosity on shear rate were increased by raising the temperature and the concentration and surface area of carbon black.

As the concentration of carbon black was increased, the viscosity at low shear rates became unbounded below a specific value of the shear stress, designated the yield stress. Similarly, from dynamic mechanical measurements, the filled polymers became increasingly non-Newtonian on the addition of carbon black, exhibiting yield at low frequency and a convergence of dynamic moduli of filled and pure polymer at high frequency. Here, the yield phenomenon is associated with frequency independent dynamic moduli at low frequencies. Both yield stresses and limiting low frequency moduli are independent of temperature and almost independent of the nature of the polymer matrix. Agglomeration of the filler and the formation of an independent network of carbon black, at low shear rates or frequencies, is inferred to prevent flow [6-9]. Moreover, the apparent viscosity of polymers filled with carbon black was sometimes lower than that of the pure polymer.

In this paper, we examine the rheological response of model filled systems. Here, the filler particles are crosslinked monodisperse polystyrene spheres. Sizes vary from 0.2 to 0.8 μm and divinylbenzene weight ratios range up to 10%.

EXPERIMENTAL DETAILS

MATERIALS

Polystyrene obtained from the Dow Chemical Company (Dow Styron 685), with a weight average molecular weight of 250,000 g/mol and a polydispersity of 2.9, from gel permeation chromatography of tetrahydrofuran solutions, is used as the matrix in our studies.

Monodisperse crosslinked polystyrene beads are prepared by persulfate initiated emulsifier-free emulsion polymerization [10]. Different crosslink densities are obtained by varying the ratio of divinylbenzene/styrene. The bead sizes used for these studies range from 0.2 to 0.8 μm , as measured by scanning electron microscopy.

Radical scavenger, 2,6-di-tert-butyl-4-methyl phenol (BHT) is 99% purity from Aldrich Chemical Company and is used to prevent thermal and mechanical degradation during melt mixing and testing [11]. In this paper, all melt mixed samples contain 0.2% BHT.

Tetrahydrofuran, HPLC grade from Fisher Scientific Company, is used as solvent for

solution mixing and chromatography. Methanol, from Fisher Scientific Company, is used to precipitate polystyrene from solution.

MIXING

Mixing of polystyrene beads and polystyrene matrix are accomplished as previously described [11]. Melt mixing is done at 175°C in an internal mixer (Brabender). A solution mixing technique involves dispersing crosslinked beads in a polystyrene solution in tetrahydrofuran, followed by coprecipitation into methanol. Also, latexes of crosslinked and uncrosslinked beads are mixed and co-coagulated. After mixing, samples are compression molded into 5 cm diameter discs, 1 mm thick, in a hydraulic press (Preco) at 175°C and 1.5×10^7 Pa for 15 minutes, and trapped air bubbles removed.

CHARACTERIZATION

Bead size and dispersion in the polystyrene matrix are assessed by scanning electron microscopy (Cambridge Instruments, Stereoscan 360) using LaB6 filament and 10kV potential. Samples were sputter coated with gold and palladium for microscopy.

The molecular weight of the polystyrene matrix and uncrosslinked beads is determined by gel permeation chromatography (GPC). GPC is conducted with a Waters (M-6000A) instrument, equipped with five microstyragel columns, or with a high performance liquid chromatograph (Perkin-Elmer Tri-Det HPLC, Series 1000 pump), equipped with a 5 μ m mixed bed organic, size exclusion column (PE/PL GEL), or another GPC (Perkin-Elmer, Series 10 pump, LC-75 Spectrophotometric Detector, 3600 Data Station) with PL Gel 5 μ m and 10 μ m mixed bed columns. The tetrahydrofuran mobile phase flow rate approximates 1.0 ml/min and ultraviolet detectors are used. The instruments are calibrated with polystyrene standards and toluene injected to normalize flow rate and chart speed.

The glass transition temperatures of beads and bead filled polystyrenes are determined by differential scanning calorimetry (Perkin-Elmer DSC-4). A thermogravimetric system (Perkin-Elmer TGS-2) is used to ascertain the thermal stability of these systems.

RHEOLOGY

A rheogoniometer (Weissenberg, Model R19) with cone and plate geometry (cone angle = 0.034 rad, plate radius = 2.5 cm) is used for steady and oscillatory shear measurements. Rheological properties, taken at 180 and 200°C, include viscosity, η , and first normal stress difference, N_1 , at various shear rates, $\dot{\gamma}$, in steady shear flow, and storage modulus, G' , loss modulus, G'' , and dynamic viscosity, η' , at different frequencies, ω , in small amplitude oscillatory shear flow. Because of the destructive nature of steady shear measurements at high shear rates, dynamic experiments are run first and the reversibility of dynamic and steady shear testing at low $\dot{\gamma}$ is assessed by repeated runs.

In order to examine the reliability of steady shear measurements using the Weissenberg rheogoniometer, the output torque from the torsion head was recorded continuously at various shear rates and stored in a computer (IBM PC-XT). The viscosity was calculated and plotted as a function of time.

RESULTS

From the continuous recording of torque at the inception of steady shear flow, growth of the shear stress was determined. For pure polystyrene and polystyrene containing 5% crosslinked beads, of various crosslink densities and sizes, the output torque increases rapidly and levels off in 10 seconds, producing a constant torque, thereafter. Here, the output torque of filled systems exceeds that of the pure polymer, although filled and pure samples are very close in torque or shear stress. However, no sign of plasticization by filler was noted [6, 7]. With 20% filler concentration, the resultant shear stress takes slightly longer to stabilize. The exact shear stress response depends on shear rate. With increasing shear rate (above 0.139 s^{-1}), shear stresses became almost independent of filler loading.

The viscosity at 200°C as a function of shear rate of polystyrene, stabilized with 0.2% BHT and melt mixed with various concentrations of $0.45 \text{ }\mu\text{m}$ monodisperse polystyrene beads, the latter crosslinked with 2% by weight of divinylbenzene (DVB) and synthesized at

80°C in a tumbling reactor [10], is illustrated in Figure 1. Similar results are obtained for polystyrene composites containing beads crosslinked with 1 and 5% DVB. The line for 40% loading has a slope of -0.44. The storage modulus, G' , and loss modulus, G'' , are plotted against frequency for this system in Figures 2 and 3, respectively. Consistent results are also observed for polystyrene composites containing beads crosslinked with 1 and 5% DVB. A comparison of the effect of different crosslink densities for steady shear measurements at 200°C for 20% loading of 0.45 μm beads is shown in Figure 4. Analogous data are obtained for storage and loss moduli in dynamic mechanical measurements at 200°C for 20% loading of these beads. The independence of rheological properties on bead crosslink density, from 1-5% DVB, is also seen at 5 and 10% loading. The steady shear viscosity and dynamic moduli for polystyrene composites filled with 0.45 μm polystyrene beads show a similar response: uncrosslinked and 0.1% crosslinked beads affect the polystyrene matrix similarly, while systems containing 1-5% crosslinked beads give higher rheological properties, that are identical to each other.

Steady shear viscosity and dynamic moduli for BHT stabilized 0.45 μm polystyrene bead filled systems are measured at 180°C, as well as at 200°C. Results at the two temperatures are completely analogous. Rheological properties increase with filler concentration, independent of crosslink density, between 1 and 5% DVB. Uncrosslinked beads and polystyrene beads crosslinked with 0.1% DVB, show smaller, but very similar, increases in rheological parameters. Rheological behavior is also compared at 200°C for polystyrene composites containing different size beads. The steady shear viscosity of polystyrene filled with 0.2 and 0.8 μm polystyrene beads, crosslinked with 2% DVB, is illustrated in Figures 5 and 6, respectively, as a function of shear rate for 5, 10, and 20% filler concentrations (by weight).

The effect of bead size on the enhancement of rheological behavior is illustrated by comparing properties of the polystyrene matrix with those of polystyrene composites,

containing 20% polystyrene beads crosslinked with 2% DVB, in Figures 7, 8, and 9. The steady shear viscosity of systems filled with 0.2, 0.45, and 0.8 μm beads is plotted against shear rate in Figure 7. Corresponding storage and loss moduli from oscillatory flow are shown in Figures 8 and 9, respectively, at various frequencies. Rheological measurements on these systems at other filler loadings, are completely consistent. Steady shear viscosities and dynamic moduli are basically independent of bead size.

The effect of bead crosslink density on the steady shear viscosity of polystyrene composites containing 10% polystyrene beads is illustrated in Figure 10 for 0.2 μm sized beads. Here, beads synthesized with from 1 to 10% DVB produce similar enhancements in viscosity. Dynamic mechanical analysis of these systems also show dynamic moduli largely independent of crosslink density.

DISCUSSION

The effect of small amounts of carbon black filler in reducing the steady shear viscosity of polystyrene and copolymers of styrene and butyl methacrylate, relative to that of the pure polymers, has been reported [6, 7]. This plasticization phenomenon was facilitated by increasing the molecular weight of polystyrene, reducing the surface area and concentration of carbon black and by increasing the temperature and shear rate. As we increased the shear rate during flow in a cone and plate geometry, the output torque could be reduced below that of the pure polymer. Plasticization occurred at similar shear rates for random copolymers and for high molecular weight polystyrene. Apparently, plasticization occurred on increasing the non-Newtonian response of the system, as well as on minimizing bonding between carbon black and polymer.

We have always been concerned that plasticization may be an experimental artifact and result from the loss of material by extrusion of polymer from the cone and plate at high shear rates or result from any instability in the output torque at high shear rates. In order to evaluate the stability of torque readings, the output torque was continuously recorded from the beginning of steady shear flow [12]. Plasticization was never observed for pure

polystyrene filled with crosslinked monodisperse beads. At low concentrations of beads, at which plasticization might have been anticipated, the output torque attained stable values in about 10 seconds and no evidence of material extrusion or instabilities in torque were noted. Since plasticization is associated with high shear rates, we concluded that further attempts to detect this phenomenon should be pursued by capillary rheometry, where the viscosity can be measured at much higher shear rates. In any case, at typical shear rates attainable in the Weissenberg rheogoniometer for steady shear flow, as well as for small amplitude oscillatory flow, plasticization was not observed for these systems. Here, the steady shear viscosity of filled systems always exceeded that of the pure matrix.

Similar to the behavior of glass spheres dispersed in a thermoplastic matrix [13], the steady shear viscosity of polystyrene containing crosslinked polystyrene beads shows a Newtonian region at low shear rates, and a power law region at high shear rates, and does not exhibit a yield stress. However, polymer systems containing ceramic particulates [13] or carbon black [4, 6-9], show a yield stress. It has been suggested that reactive fillers may agglomerate, within the filled composite, forming an independent network that prevents flow, until a specific yield stress is exceeded. For polystyrene filled with crosslinked monodisperse polystyrene beads, the viscosity increases with bead concentration, producing a series of almost parallel curves of viscosity versus shear rate from 0-30% loading (Figure 1). At 40% loading, the response to steady shear flow is non-Newtonian over the entire range of shear rates measured--giving a linear or power law relation. However, the slope is much too low (absolutely) to indicate yield. A yield stress would be associated with a slope of -1, on the double logarithmic plot of steady shear viscosity against shear rate, as the shear stress becomes independent of shear rate and the viscosity increases as the shear stress is reduced, and becomes unbounded below a constant shear stress--the yield stress.

In order to display a uniformly increasing steady shear viscosity with filler loading, 0.2% BHT antioxidant is added to suppress thermomechanical degradation [11]. Models of the shear viscosity of highly filled suspensions have been proposed [13, 14]. In agreement

with literature [15], the steady shear viscosity increased with volume fraction of inert filler, for liquid suspensions, displaying non-Newtonian behavior. Similarly [15], increases in dynamic moduli with filler loading are observed in oscillatory flow. For pure polystyrene and for samples filled with up to 40% crosslinked polystyrene beads, systems exhibit a linear response, on a logarithmic scale, at low frequencies, with log dynamic moduli linear with log frequency. The values of limiting low frequency slopes on the storage and loss moduli curves (Figures 2 and 3) are tabulated in Table 1. For the double logarithmic plot of storage modulus against frequency, the slope approximates 1.3 at low frequencies, both for pure polystyrene and a polystyrene composite containing 5% monodisperse crosslinked polystyrene beads at 200°C. We have reported such slopes for several pure polymers [8, 9]. The initial slopes of storage modulus curves for polystyrene decreased from 1.72 to 1.52 at 200°C, on increasing the molecular weight. Since the molar mass of polystyrene used in these studies, $\overline{M}_w = 250,000$ [11], exceeded the higher one reported, $\overline{M}_w = 210,000$ [8], it is not surprising, that the slope of G' was reduced to 1.3. With increasing concentrations of filler, the slope of G' drops, as the filled composites deviate further from Newtonian behavior and a predicted slope of 2 [8, 16, 17].

The initial slope of the loss modulus decreases from the Newtonian value of 1 [8, 16, 17], with increasing molar mass. As a result, we observe slopes approximating 0.9, almost independent of bead concentration. However, at very high concentrations of beads, 30 and 40% by weight, the slopes of G'' curves are reduced further, signifying large deviations from Newtonian behavior. At 40% filler loading, the large drop in slope of low frequency moduli may signify an approach to the yield phenomenon. Typical of non-Newtonian systems, the dependence of moduli on frequency decreases at higher frequency.

Using 0.45 μm polystyrene beads crosslinked with 1 to 5% divinylbenzene, steady shear (Figure 4) and oscillatory flows appear to be independent of the crosslink density of the beads. Although these beads vary in glass transition temperatures [10], melt flow

measurements at 180 and 200°C are made well above T_g . However, uncrosslinked beads and beads crosslinked with 0.1% divinylbenzene, exhibit reduced rheological response (Figure 4). During high shear mixing of the beads in the polystyrene matrix at elevated temperatures, the uncrosslinked beads are melted and a compatible blend of polystyrenes results. Since the molar mass of the beads exceeds that of the matrix [11], the viscosity and dynamic moduli are elevated. Morphological studies of these composites by scanning electron microscopy indicate that polystyrene beads crosslinked with 0.1% divinylbenzene did not preserve their spherical shape following melt mixing. In fact, such beads appear to be extensively destroyed by mechanical dispersion. Although crosslinked, to the extent that such beads are insoluble, the crosslink density was not high enough to prevent bead collapse during melt mixing. That the viscosity and moduli enhancements are indistinguishable from uncrosslinked beads is probably fortuitous, and results from a reduction in hydrodynamic radius on crosslinking and small overall increases in rheological parameters. The independence of steady shear viscosity on crosslink density was obtained at least up to 10% divinylbenzene (Figure 10).

Similar increases in rheological properties with filler content were noted (Figures 5 and 6) for both 0.2 and 0.8 μm polystyrene beads. At the higher shear rates, the steady shear viscosity becomes less dependent on filler loading and the viscosity/shear rate curves converge. For beads ranging in size from 0.2 to 0.8 μm diameter, the rheological properties in steady shear and oscillatory flows are independent of bead size (Figures 7-9). The steady shear viscosity of suspensions of monodisperse silica particles, varying in diameter from 56 to 220 nm, and in which a stabilizing layer of octadecyl chains is grafted onto the particle surface, has been reported [18]. Low and high shear limiting viscosities were shown to be independent of particle size, and depended only on volume fraction.

CONCLUSIONS

The rheological behavior of polystyrene containing monodisperse sized crosslinked polystyrene beads has been studied by rheogoniometry in steady shear and in small amplitude oscillatory flows. The polystyrene systems are non-Newtonian and exhibit shear rate dependent viscosities and "nonlinear" dynamic moduli. The viscosity and moduli of bead filled polystyrene always exceeded those of the pure polystyrene matrix. From a continuous recording of stress growth upon inception of steady shear flow, plasticization was not observed at shear rates up to 5 s^{-1} , on inclusion of crosslinked beads.

Polystyrene composites containing monodisperse polystyrene beads, crosslinked with 1-10 weight percent divinylbenzene and ranging in diameter from 0.2 to 0.8 μm , show steady shear viscosities and dynamic moduli at 180 and 200°C, that increase with the volume fraction of beads, but are independent of bead size and crosslink density. The steady shear viscosity, of filled systems containing up to 30% polystyrene beads, exhibits a Newtonian region, at low shear rates, and a power law region, at higher shear rates. At a concentration of 40% beads, the steady shear viscosity shows a power law behavior only, and no yield stress. For the polystyrene composites, storage and loss moduli, from dynamic mechanical analysis, are linear with frequency, on a double logarithmic plot, at low frequencies, displaying limiting slopes of 1.3 and 0.9, respectively. At high concentrations of beads, the low frequency slopes of dynamic moduli decrease. The dependence of dynamic moduli on frequency decreases at high frequency. Filled polystyrene composites, containing uncrosslinked polystyrene beads or beads crosslinked with 0.1% divinylbenzene, exhibit reduced rheological response compared to systems containing more highly crosslinked beads. Uncrosslinked beads and beads crosslinked with 0.1% divinylbenzene are destroyed by thermomechanical dispersion in the melt.

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Table I. Slopes of Dynamic Mechanical Moduli

Loading %	SLOPE	
	G'	G''
Pure PS	1.27	0.91
5	1.30	0.92
10	1.20	0.92
20	1.20	0.90
30	1.15	0.86
40	0.88	0.73

LIST OF FIGURES

FIGURE

1. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with various concentrations of crosslinked polystyrene beads (2% DVB, 0.45 μm size).

- pure polystyrene
- × 5 weight % beads
- △ 10 weight % beads
- 20 weight % beads
- ▲ 30 weight % beads
- + 40 weight % beads

2. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of polystyrene composites from Figure 1.

3. Loss modulus (G'') at several frequencies (f) from dynamic mechanical analysis of polystyrene composites from Figure 1.

4. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with 20% by weight of 0.45 μm polystyrene beads varying in crosslink density.

- pure polystyrene
- ▲ uncrossed beads
- + beads crosslinked with 0.1% DVB
- × beads crosslinked with 1% DVB
- △ beads crosslinked with 2% DVB
- beads crosslinked with 5% DVB

5. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with various concentrations of crosslinked polystyrene beads (2% DVB, 0.2 μm size).

- pure polystyrene
- × 5 weight % beads
- △ 10 weight % beads
- 20 weight % beads

6. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with various concentrations of crosslinked polystyrene beads (2% DVB, 0.8 μm size).

- pure polystyrene
- × 5 weight % beads
- △ 10 weight % beads
- 20 weight % beads

7. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with 20 weight % crosslinked (2% DVB) polystyrene beads of varied size.

- pure polystyrene
- × 0.2 μm beads
- △ 0.45 μm beads
- 0.8 μm beads

8. Storage modulus (G') at several frequencies (f) from dynamic mechanical analysis of polystyrene composites from Figure 7.

9. Loss moduli (G'') at several frequencies (f) from dynamic mechanical analysis of polystyrene composites from Figure 7.
10. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with 10% by weight of 0.2 μm polystyrene beads varying in crosslink density.
- pure polystyrene
 - × beads crosslinked with 1% DVB
 - △ beads crosslinked with 2% DVB
 - + beads crosslinked with 5% DVB
 - beads crosslinked with 10% DVB

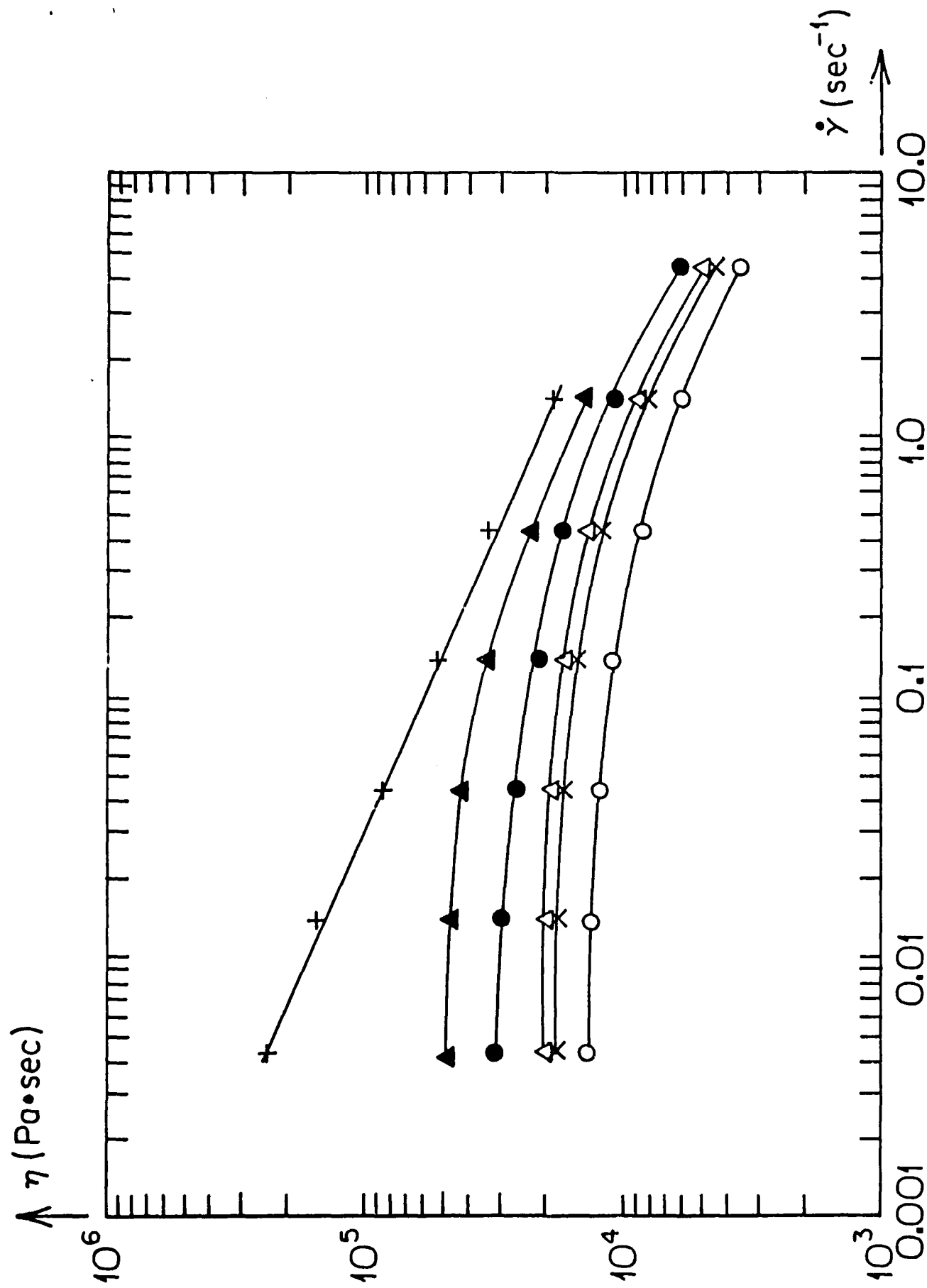


FIGURE 1

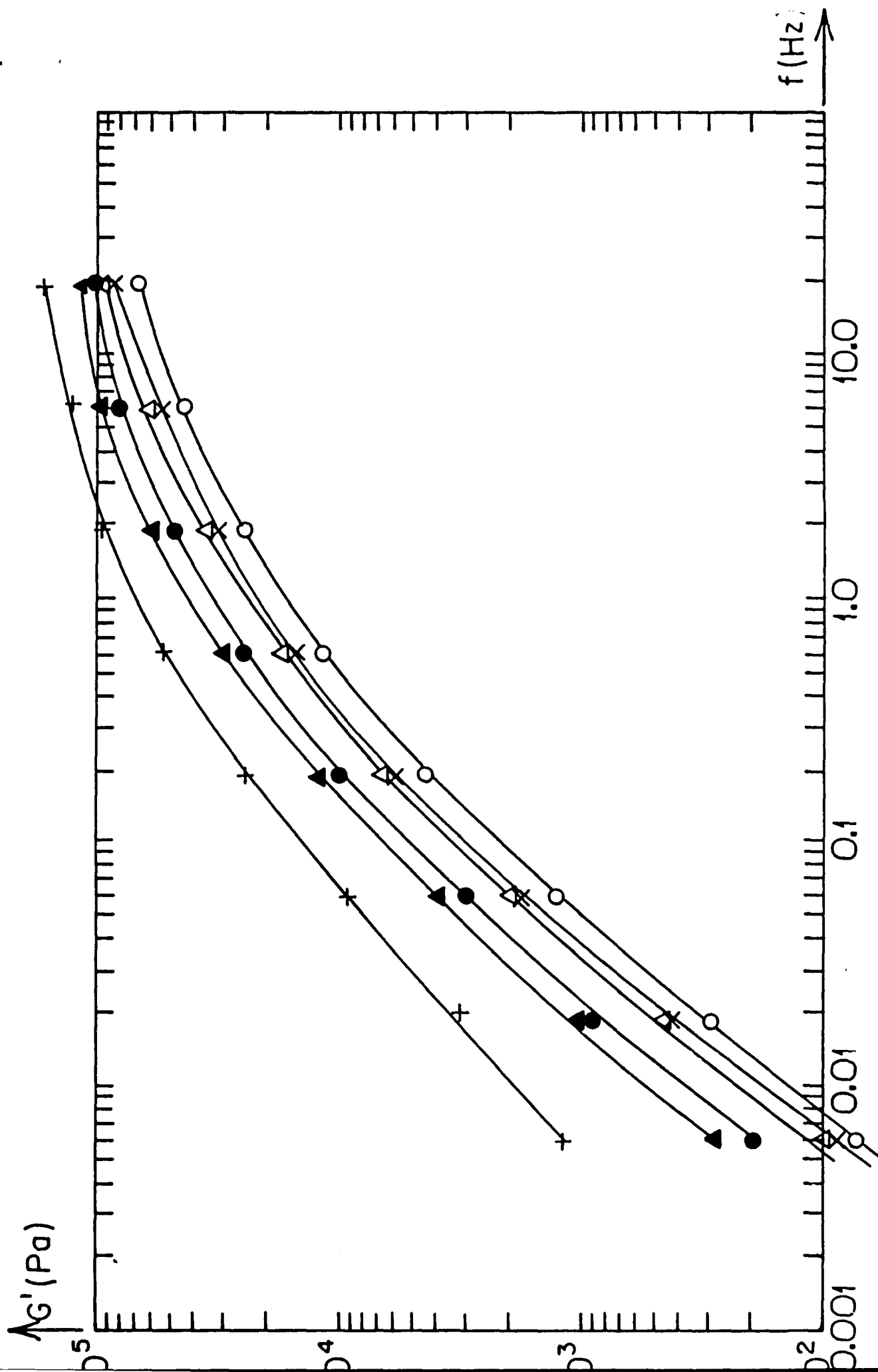


FIGURE 2

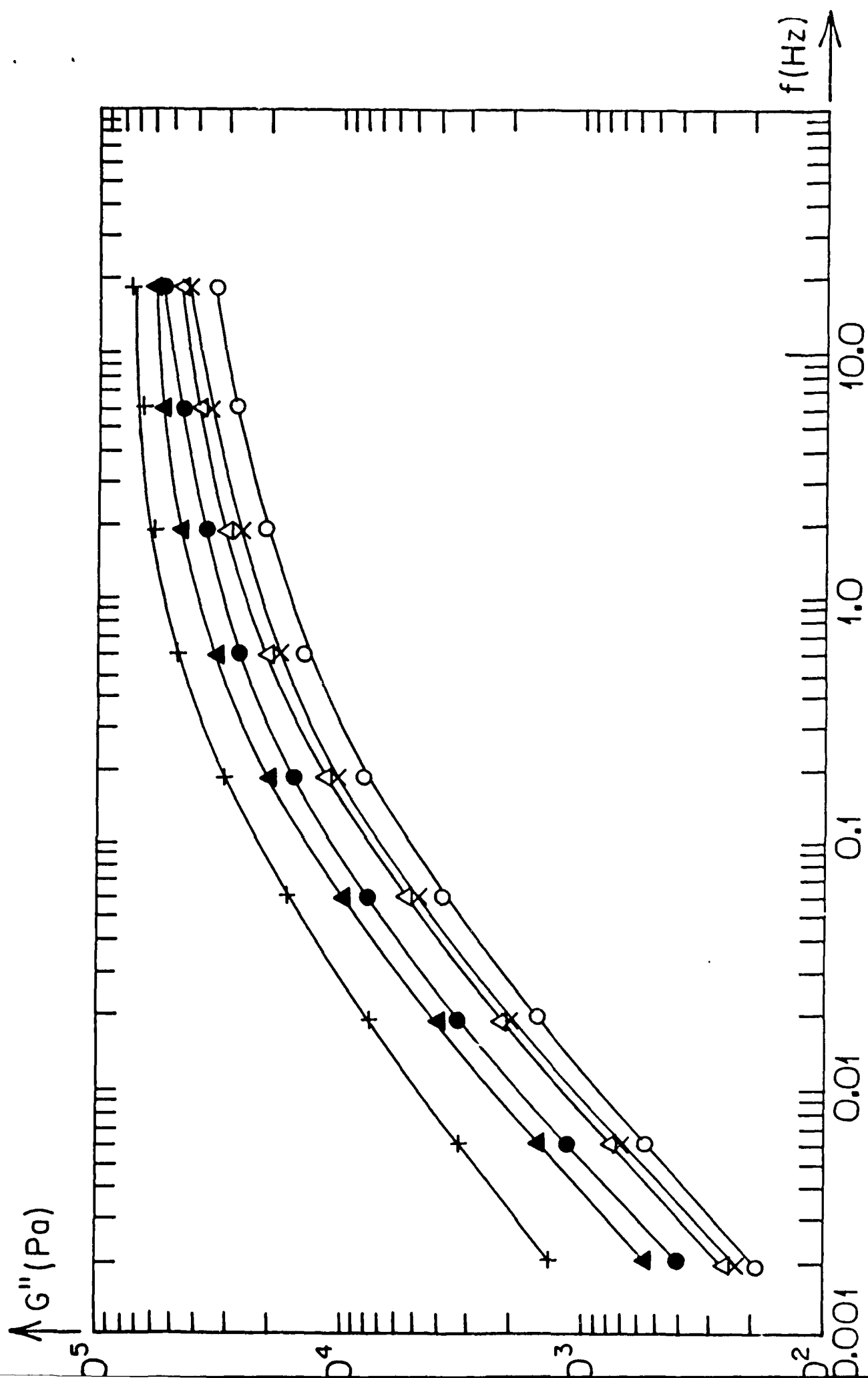


FIGURE 3

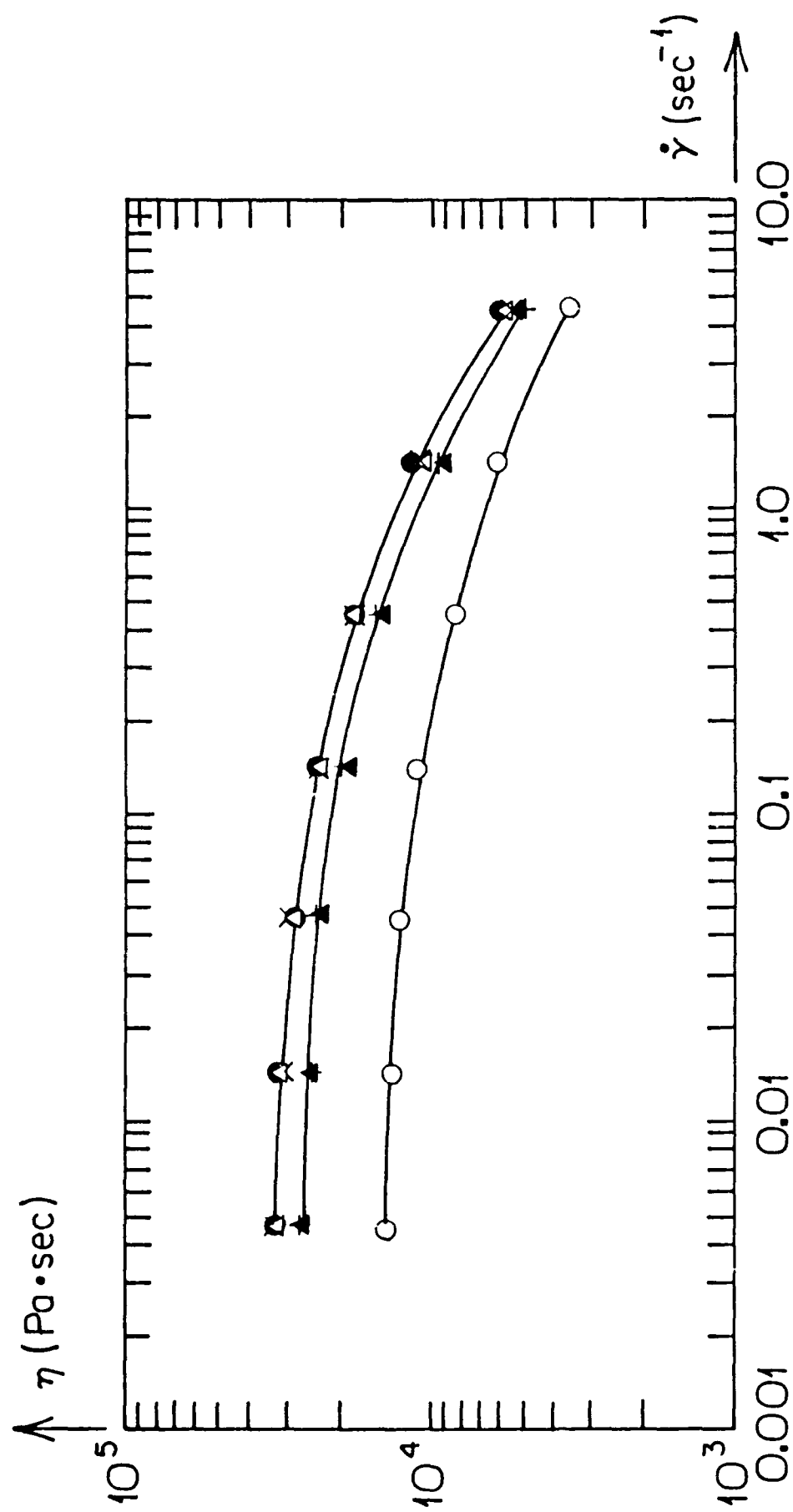


FIGURE 4

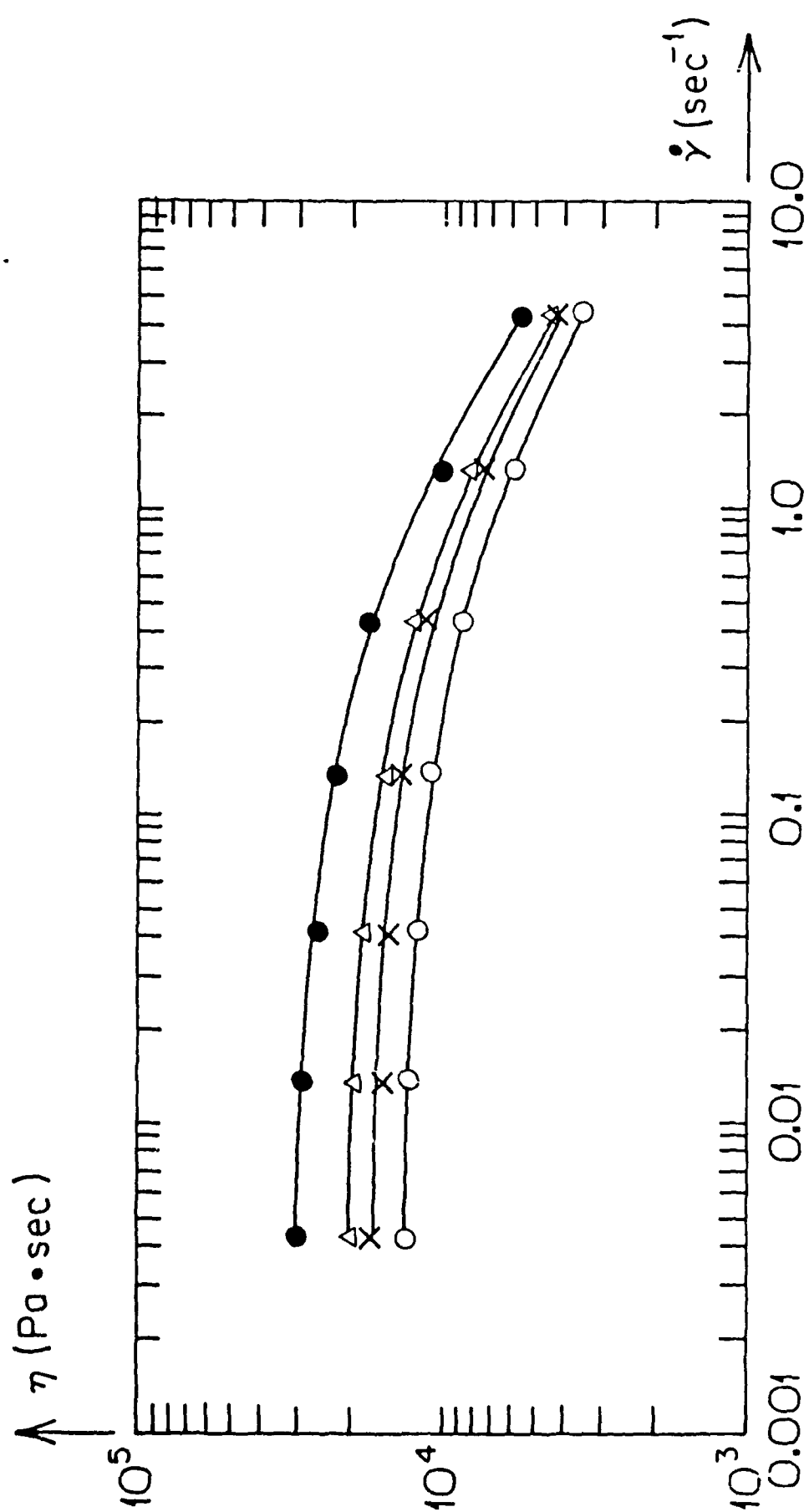


FIGURE 5

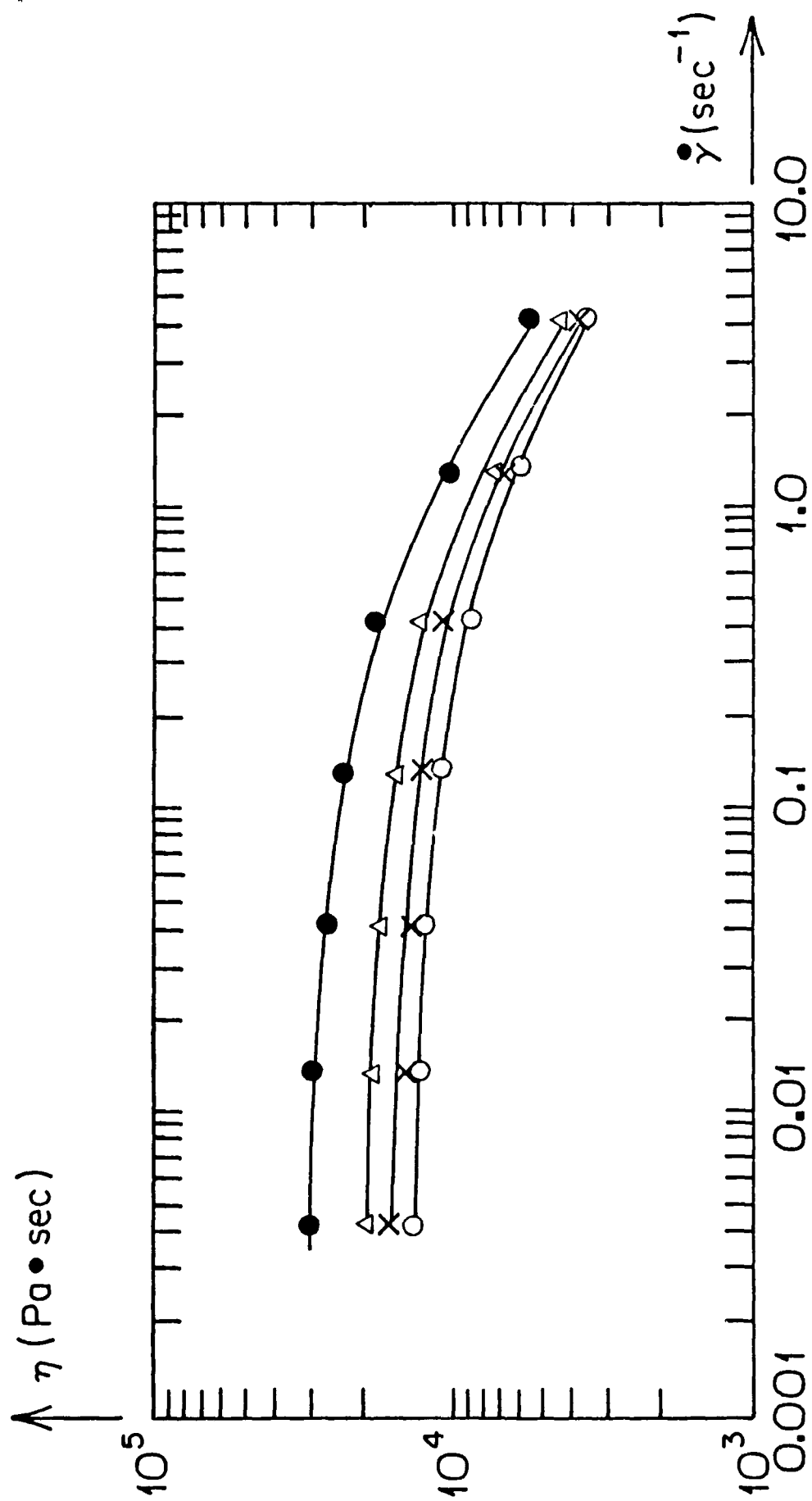


FIGURE 6

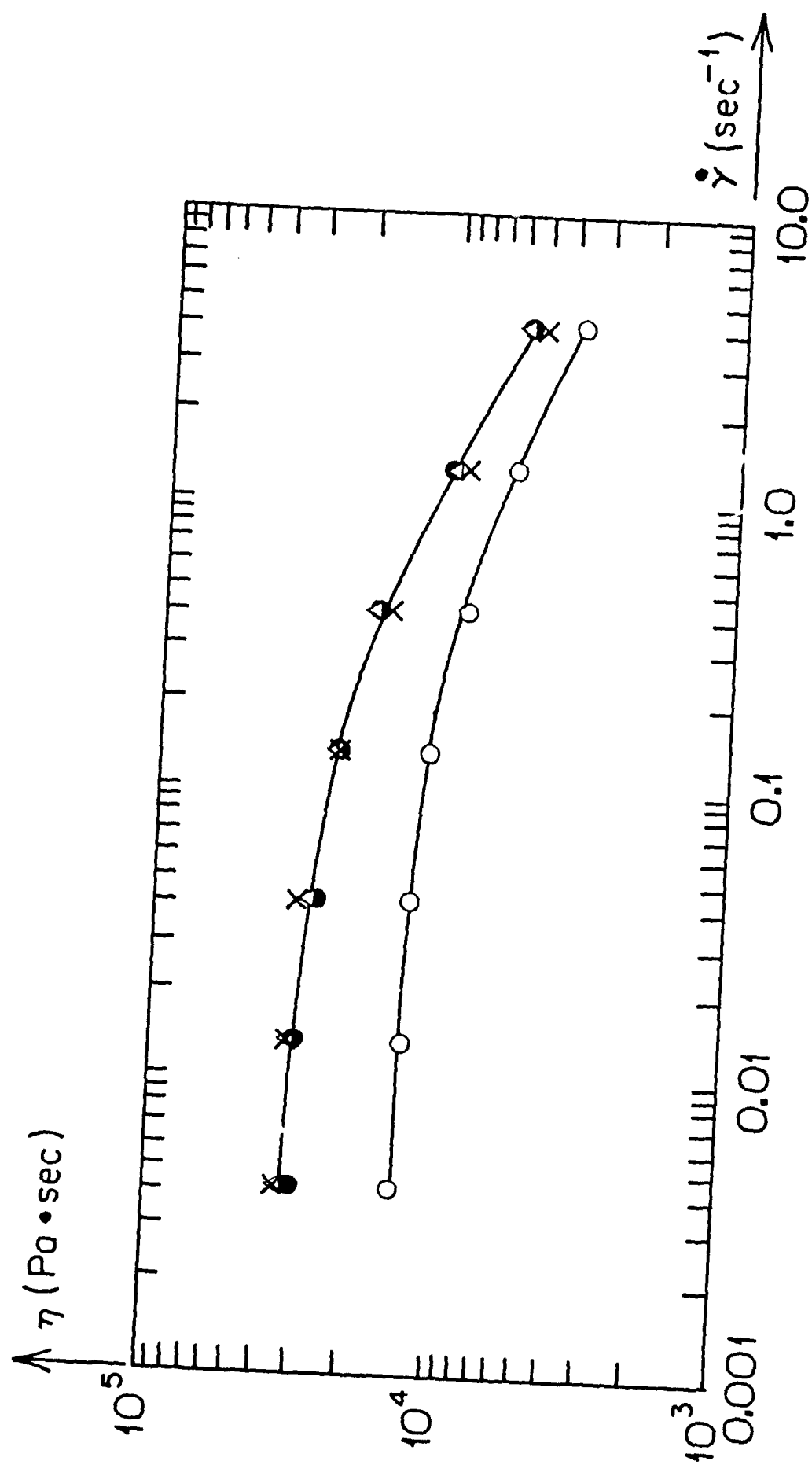


FIGURE 7

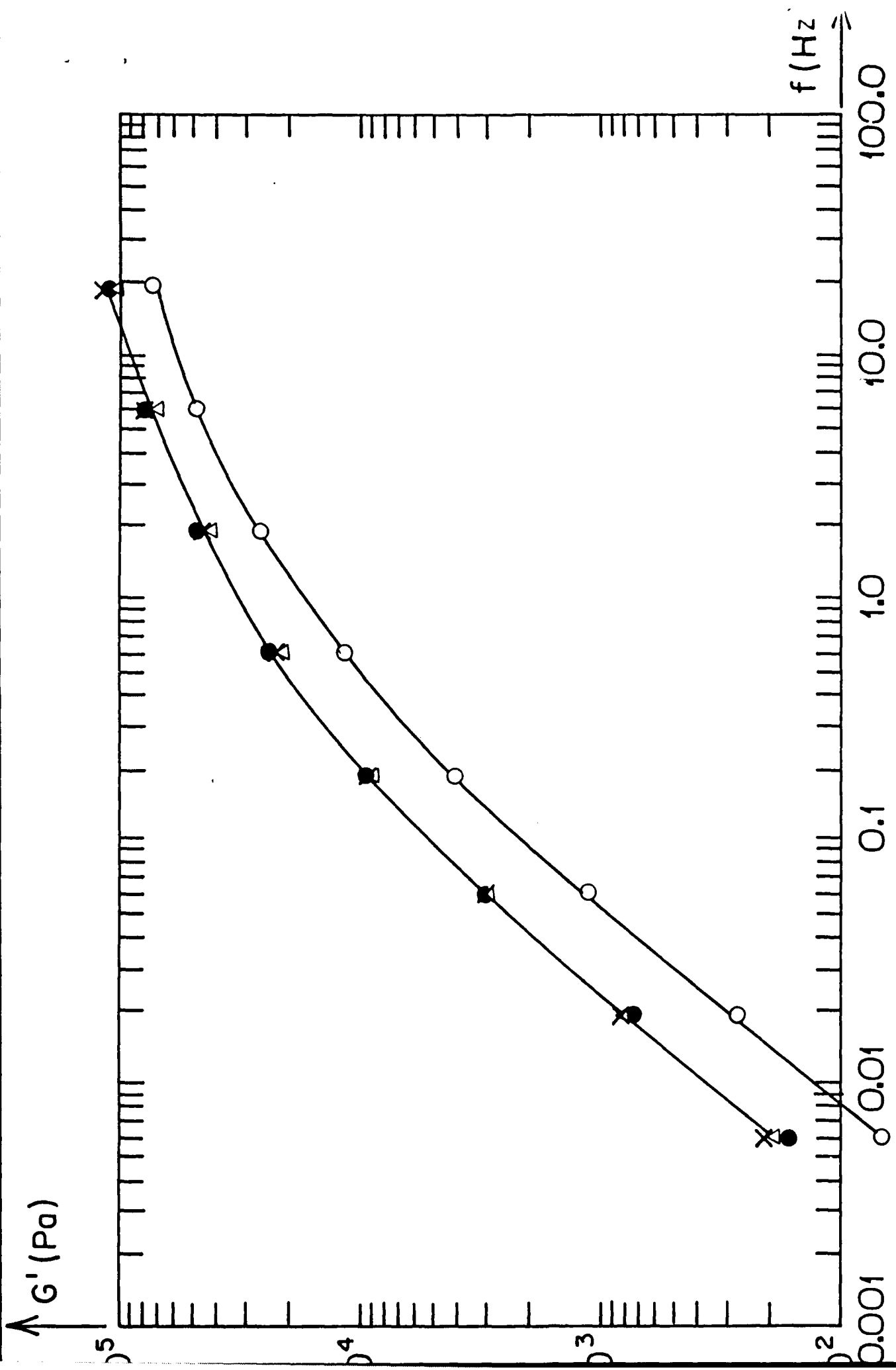


FIGURE 8

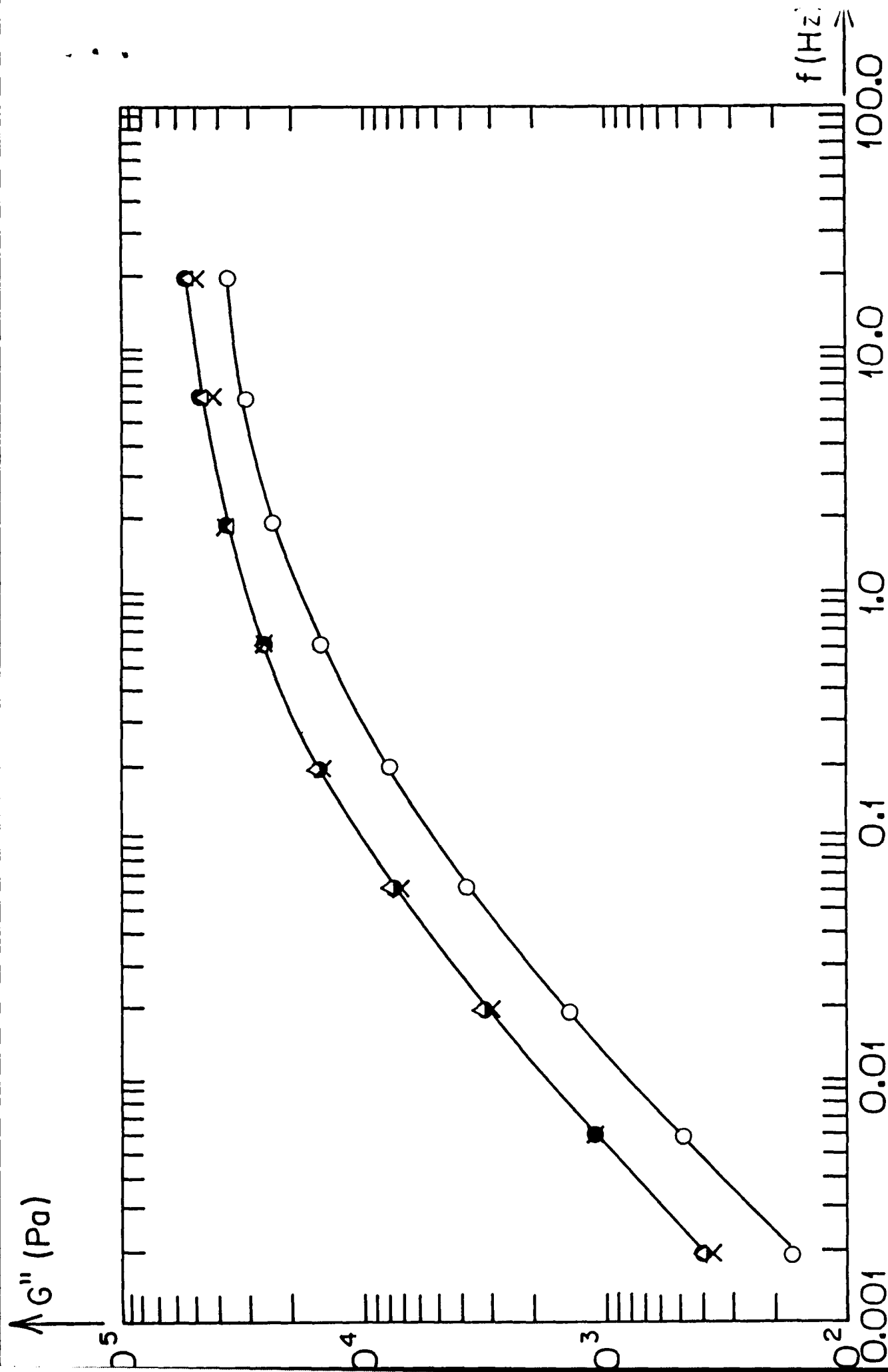


FIGURE 9

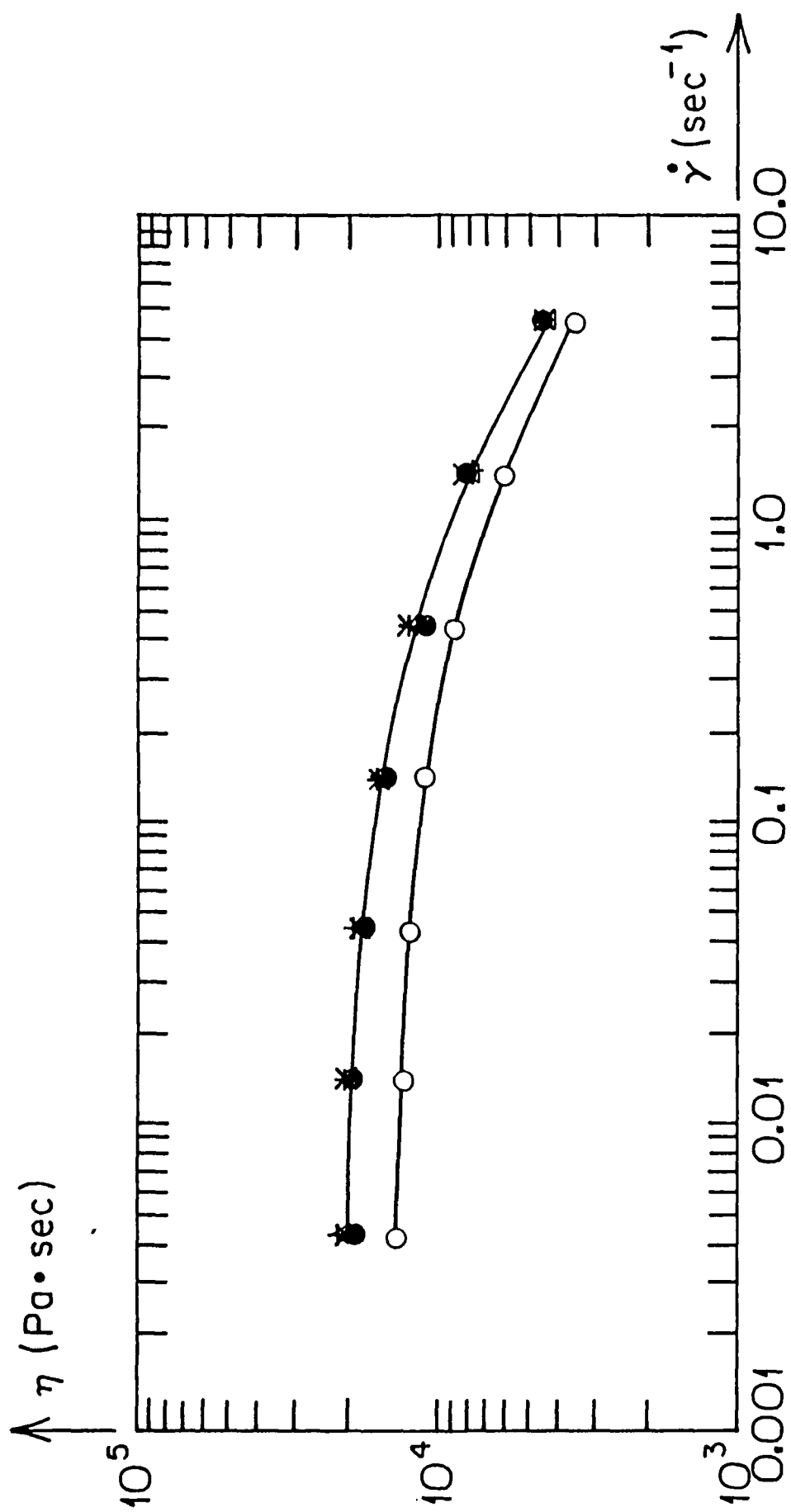


FIGURE 10

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